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Inhibition of the thermal polymerization of styrene

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INHIBITION OF THE THERMAL POLYMERIZATION OF STYRENE

by

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Approved by Howard E. Sluffer

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INTRODUCTION

The purpose of this work is to study the rate of reaction and mechanism of various inhibitors in the thermal, uncatalyzed polymerization of styrene. Other attempts have been made to study the inhibitory process, the most recent[1] making use of a dilatometer to measure volume changes during the course of polymerization. However, this method, and others, represents indirect means of study. The spectrophotometric method of study presented here, offers a simple and direct method for determining the rate of disappearance of an inhibitor in the inhibition process, and also affords a method of calculating the rate constants for the initiation stage of polymerization. This method however, has its limitations. Only inhibitors which are colored in solution and which lose their color during the inhibition process, can be sucessfully studied, since all spectrophotometric measurements are made in the visible spectrum. Some of the family of compounds known as quinones come in this category. The method was tried unsuccessfully on a nitroso compound, p-nitrosodimethylainline.

The work is divided into two main parts; one dealing with a studyof p-benzoquinone, the other a study of chloranil (tetra chloroquinone). Each study is further divided into spectrophotometric measurements and viscosity measurements. The purpose of the viscosity data is to correlate and validate the basic assumptions made.

ACKNOWLEDGEMENT

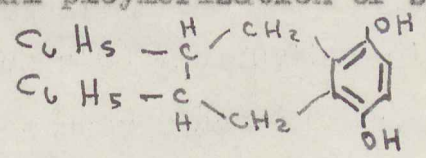
The author is highly indebted to Dr. Howard E. Sheffer for his invaluable assistance in explaining the experimental data and for his advice in laboratory technique. Acknowledgment is also made to the Schenectady Varnish Company who sponsored this research and provided the chemicals and necessary apparatus.

DISCUSSION

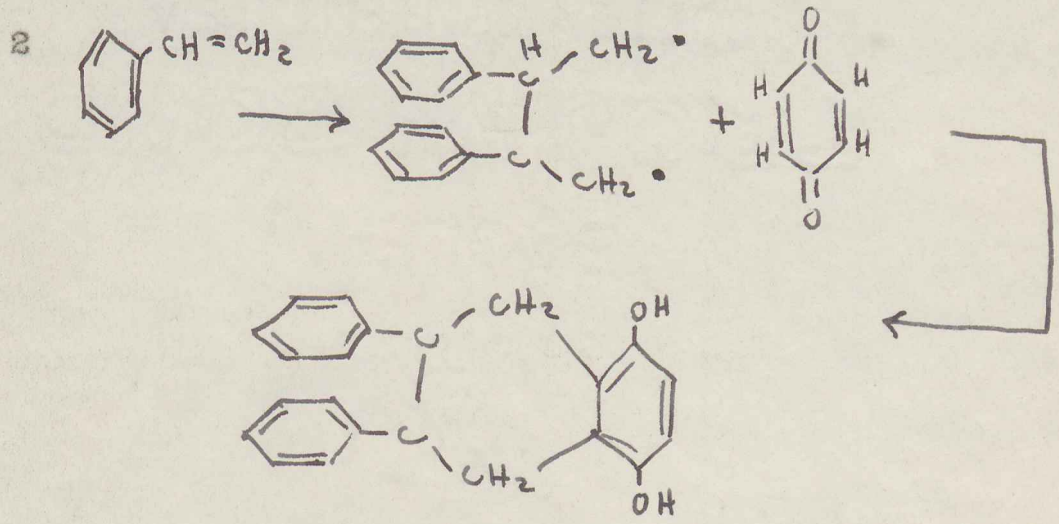
PART I- Theoretical Qualitative Discussion of Inhibitors

Foord[2] has defined an inhibitor as a substance which temporarily prevents polymerization from taking place, during a so called "induction period", but which allows polymerization to proceed at its normal rate after the inhibitor has been used up. Retarders are defined by Foord as substances which do not prevent polymerization but which merely slow down the rate of polymerization. p-benzoquinone has been classed by Foord as an inhibitor, based upon viscosity data. Foord observed during the course of the polymerization, the quinone gradually lost its color, and finally became colorless at the presumed end of the inhibition process. It was this observation which became the basis for this work. It was reasoned that if the color change was due only to the inhibitor (quinone) taking part in the inhibitory process, then by spectrophotometric measurement, a simple and direct method of determining the order of the inhibitory process was offered.

Much work of late has been done concerning the nature of the inhibitory process and the nature of the end products formed during the inhibition reaction. Breitenbach and Breitenbach[3] have offered good evidence that the end product formed during the uncatalyzed thermal ploymerization of styrene, using benzoquinone as an inhibitor, is



Kern[4], working on the assumption that this actually is the end product formed during the inhibition process, postulated that this end product is formed by the following mechanism, in which styrene forms a diradical



Harman and Eyring[5], in an attempt to corroborate the theory of Kern, have offered two mechanisms, based upon quantum mechanics, by which the double bond of the styrene molecule may become activated to form the diradical.

PART II- Development of Kinetic Equations for Thermal Polymerization

The polymerization process may be divided into four basic stages; Initiation, in which free radicals are formed; Propagation, in which the newly formed free radicals react with molecules of the monomer to form a growing chain; chain Transfer, in which a free radical may be transferred from one molecule to another,

resulting in shorter chains, and lower molecular weight polymers; and Termination, the process where free radicals are "deactivated" to form stable products. The "deactivation" may be accomplished by two free radicals interacting to form a stable product or by the free radicals reacting with molecules of some other substance to form a stable product (inhibition). Represented mathematically, the four stages are

(a) Initiation:

$$2M \xrightarrow{K_1} M^*$$

(b) Propagation:

$$M + M^* \xrightarrow{K_2} M\text{-}M^*$$

(c) Chain Transfer:

$$M^* + N \xrightarrow{K_3} M + N^*$$

(d) Termination:

1. $M^* + M^* \xrightarrow{K_4} M\text{-}M$ (Stable Product)

2. $nM^* + m\varphi \xrightarrow{K_4'} X$ (Stable Product)

M = Monomer

M^* = free radical

K = rate constant

N = Some other molecule (solvent, monomer, etc.)

φ = inhibitor

X = Stable product

n = number of free radicals

m = number of molecules of inhibitor

For polymerization carried out without a catalyst (thermal polymerization), it has been generally observed that the initiation process is a second order reaction with respect to the monomer. If the initiation envolves a bimolecular dimerization of the monomer[6], then the rate of initiation is proportional to the square of the monomer concentration

$$(1)\quad \frac{d[M^*]}{dt} = \text{rate of initiation} = K_1[M]^2$$

and the rate of termination of chain growth would be proportional to the square of the free radical concentration.

(2) $\text{rate of termination} = K_4 [m^*]^2$

Then, at equilibrium,

(3) $K_1 [m]^2 = K_4 [m^*]^2$

(4) $[m^*] = \left(\frac{K_1}{K_4}\right)^{1/2} [m]$

In other words, the concentration of the free radical is a function of the monomer concentration. From stage (6), the propagation stage, the rate of propagation is expressed by

(5) $-\frac{d[m]}{dt} = \text{rate of propagation} = K_2 [m][m^*]$

(6) $-\frac{d[m]}{dt} = K_2 [m] \left(\frac{K_1}{K_4}\right)^{1/2} [m]$

$= K_2 \left(\frac{K_1}{K_4}\right)^{1/2} [m]^2$

If we consider the termination stage to be the resultant of the two possible means of cessation, then the following equation would be true:

(7) $-\frac{d[m^*]}{dt} = K_4 [m^*]^2 + K_4' [m^*]^n [\varphi]^m$

(8) $\frac{d[m^*]}{dt} = K_1 [m]^2 - K_4 [m^*]^2 - y K_4' [m^*]^n [\varphi]^m$

Where y represents the number of growing chains stopped by a molecule of inhibitor. The term $K_4 [m^*]^2$ can be neglected, since the amount of termination accounted for by the enteraction of free radicals, does not exceed 4% of the total at any time[1]. Thus, the simplified equation becomes deactivation. For steady state equations (where $\frac{d[m^*]}{dt} = 0$)

$$(9)\quad \frac{d[m^*]}{dt} = k_1[m]^2 - y\,k_4'[m^*]^n[Q]^m = 0$$

OR

$$(10)\quad [m^*] = \left(\frac{k_1[m]^2}{y\,k_4'[Q]^m}\right)^{\frac{1}{n}}$$

According to the current theory of inhibitors, the inhibitor loses its power as it removes chain carrying free radicals. Thus, if an inhibitor is capable of stopping "y" growing chains, it should disappear from solution at a rate equal to $\frac{1}{y}$ times the rate of chain initiation. If we assume that the inhibition is the only factor in the disappearance of quinone (and this is the basic assumption that we have made), and if we further assume that during the induction period, the monomer concentration remains essentially constant, then we can derive an expression for the inhibitor concentration, as a function of time which enables the rate constant for the initiation stage of polymerization to be determined. Thus, from stage (d), equation (1)

$$-\frac{dQ}{dt} = k_4'[m^*]^n[Q]^m \quad \text{assuming } n+m \text{ order.}$$

But we know:

$$[m^*] = \left(\frac{K_1}{y K_4'} \frac{[m]^2}{[Q]^m} \right)^{\frac{1}{n}}$$

therefore:

$$(12) \quad -\frac{dQ}{dt} = K_4' \left(\frac{K_1}{y K_4'} \frac{[m]^2}{[Q]^m} \right)^{\frac{1}{n}} [Q]^m$$

$$-\frac{dQ}{dt} = \left(\frac{K_1}{y} [m]^2 \right)^{\frac{1}{n}}$$

Matheson and coworkers[7] have concluded that m=n-1, and so equation (12) becomes

$$(13) \quad -\frac{dQ}{dt} = \frac{K_1}{y} [m]^2$$

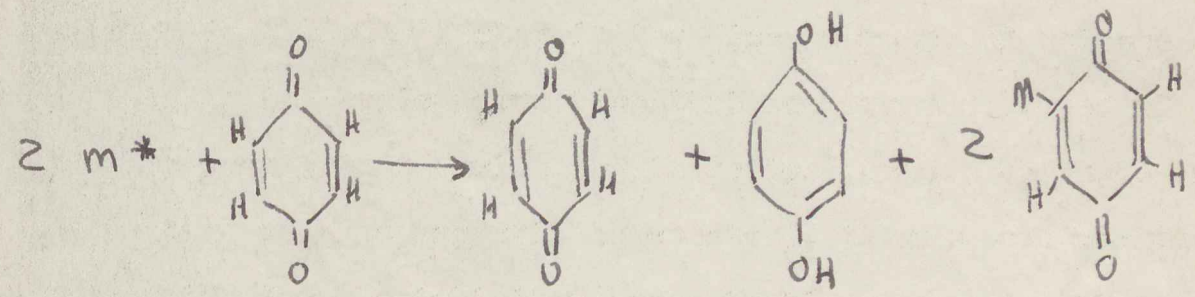
Integrating:

$$\int_{Q_0}^{Q} dQ = \int_{t_0=0}^{t} \frac{K_1}{y} [m]^2 dt$$

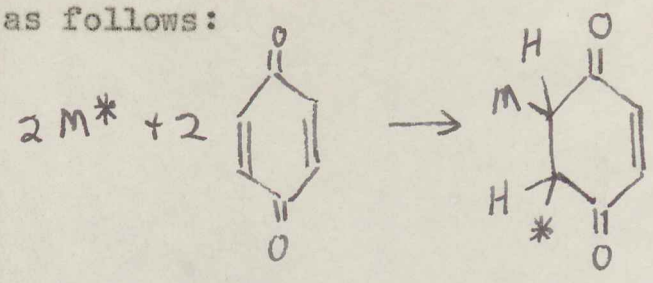
thus: $$(16) \quad Q = Q_0 - \frac{K_1}{y} [m]^2 t$$

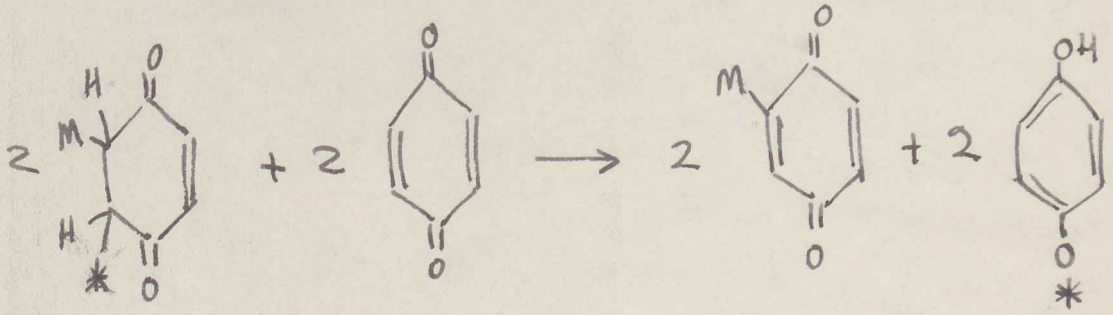
Evidence points to the fact that "y" has two probable values, one or two. However, since the aim of this work is to calculate as accurately as possible, the value of k, (the rate constant for the initiation stage), it seems worthwhile to derive a more applicable value for "y". In deriving this value for "y", a somewhat different interpertation of the formation of end products will be adopted. However, this in no way alters the basic assumptions made nor does it affect the derivation of equation (16) because the rate determining step is assumed to be the first one of the following sequence.

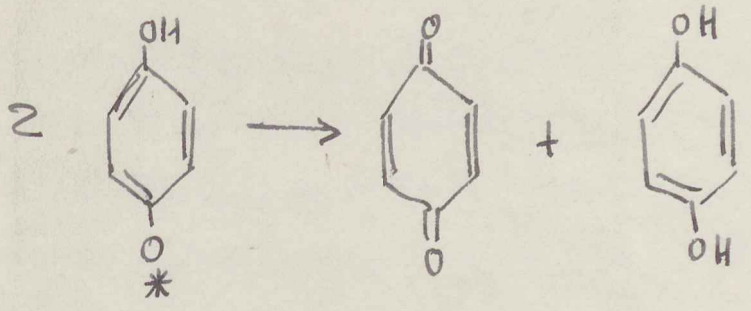
Price[9] has suggested that the reaction of a free radical with benzoquinone occurs as follows:



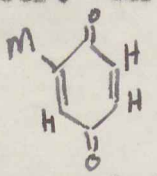
Price[9] has suggested that the mechanism for p-benzoquinone is as follows:







From this it becomes possible to determine the value of "y", which represents the number of growing chains stopped by one molecule of inhibitor. In the above reactions



might just as well be converted to a carbon substituted

hydroquinone, so that for each two radicals, one p-benzoquinone molecule is lost. The limit to the number of free radicals that combine with a quinone molecule is not the number of positions available in p-benzoquinone for substitution, but the fact that one hydroquinone of some structure, is obtained, by some mechanism, as an end product for each two radicals.

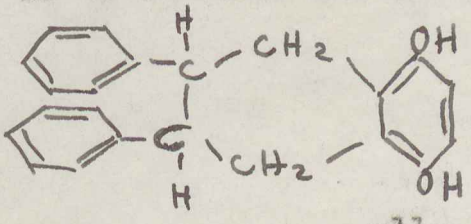
Thus, "y" seems to have a value of two, or two free radicals are stopped by one p-benzoquinone molecule.

PART III - Discussion of Experimental Results

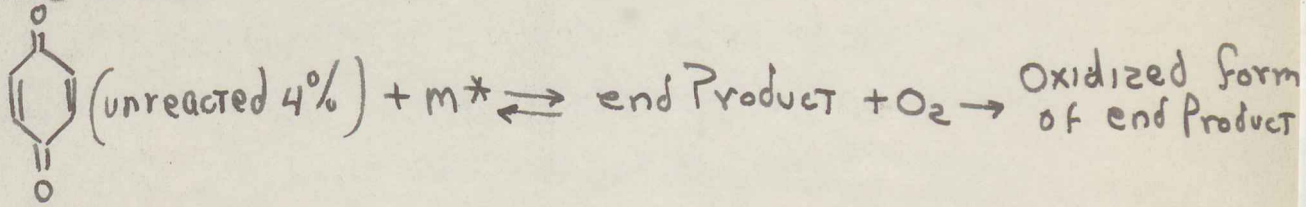
Section A - Benzo Quinone as an inhibitor

When p-benzoquinone is used as an inhibitor in the thermal polymerization of styrene, the concentration decreases linearly as a function of time. (see graphs 1,2,3,4,5,6) By interpolation of the plotted valves, the induction period can be determined relatively accurately. By comparing the induction periods of p-benzoquinone in styrene for air and vacuum, it seems as if oxygen contributes to the inhibition of polymerization. Two possible explanations are offered:

(1) if we consider the end product to be

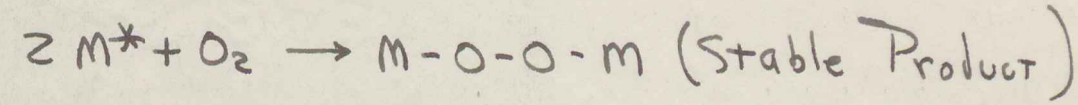


then oxygen might very weal oxidized this product to a quinone type structure, which in itself would act as an inhibitor. It has been observed (see data sheet) that not all of the p-benzoquinone is used up, but only about 96% at the end of the induction period, thus, an equilibrium may exist in the following manner

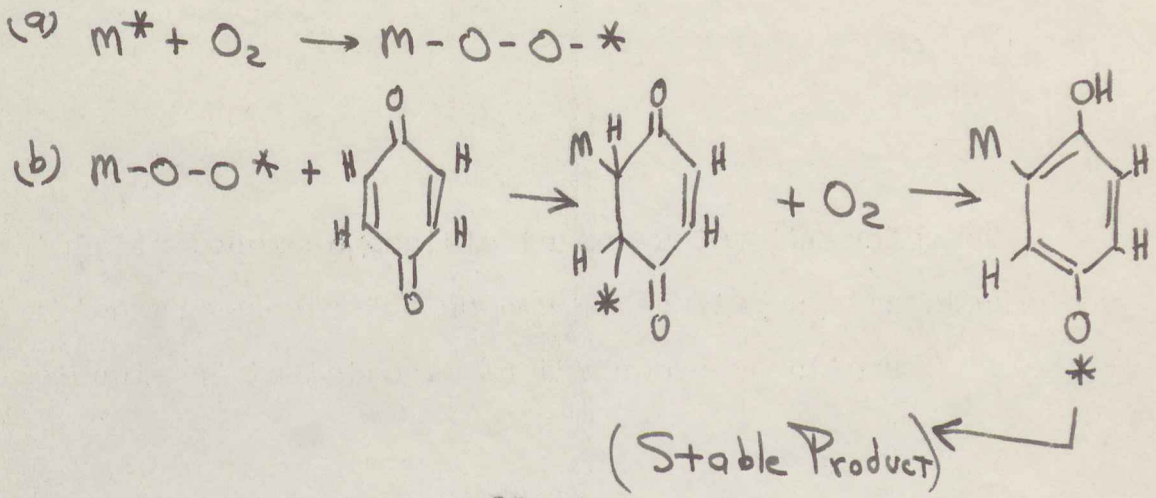


It has been calculated that equivalent amounts of oxygen and end product are present

(2) Another possible explanation for the inhibitory effect of oxygen, lies in a recent theory that free radicals are terminated in the presence of oxygen by



The suggested reactions for quinone and oxygen acting as inhibitors simultaneously are:



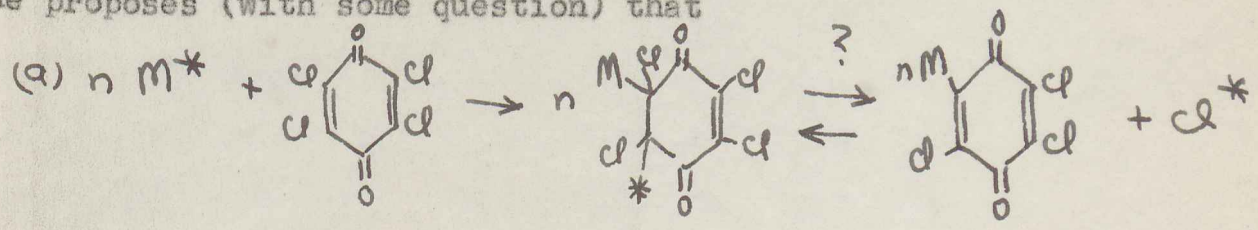
However, there exists the possibility of still another reaction occurring:

(c) $M\text{-}O\text{-}O^{*} + M^{*} \rightarrow M\text{-}O\text{-}O\text{-}M$ (Stable Product)

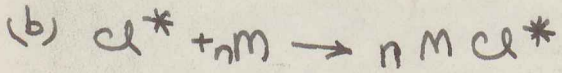
Going on the evidence of increased induction period in the presence ofoxygen, it is suggested that reaction (a) is very fast, and (b) and (c) are taking place simultaneously and at the same rate. Very little of the inhibition takes place by (d) since reaction (a) is fast. This is the second possible explanation for the increased induction period with oxygen.

Section B - Chloranil

Although chloranil in vacuum disappears linearly as a function of time, as does p-benzoquinone, Price[9] has suggested that chloranil acts as a chain transfer agent. He proposes (with some question) that



(a) $n\,M^{*} + Cl_2C_6O_2 \rightarrow n \rightarrow \overset{?}{\rightleftharpoons} nM + Cl^{*}$



(b) $Cl^{*} + nM \rightarrow nMCl^{*}$

In other words, Price offers that chloranil acts as a chain transfer agent, but the possibility of it existing as an inhibitor cannot be denied.

The results of the viscosity experiments (see figure 5) point to support of the chain transfer theory. In bath chloranil runs, air and vacuum, it was observed that the viscosity did not increase at or near the end of the induction period, as was the case with p-benzoquinone, but instead, large viscosity increases were not noticed until several hours after the induction period was apparently over. Sheffer has suggested that in the case of p-benzoquinone, there are relatively few free radicals present just after the induction period, and the viscosity would be expected to increase rapidly from this point on. However, with chloranil, after

the induction period is over, there would be present not only the relativly few monomer free radicals but also the chlorine free radicals. Thus, the viscosity would be expected to build up at a slower rate.

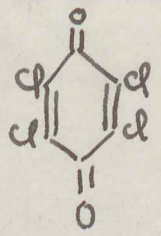
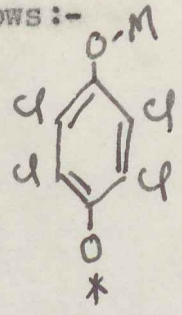
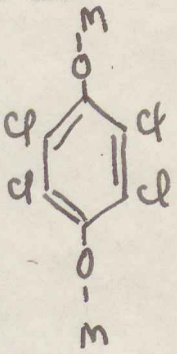
However, the data obtained for chloranil runs in air and vacuum runs pose an interesting problem. Graph (9) indicates that chloranil disappears linearly as a function of time, as does p-benzoquinone. In fact, the induction period of p-benzoquinone in vacuum and chloranil in vacuum are close enough to be within the limits of experimental error. This would indicate that chloranil acts as an inhibitor in a vacuum. If chloranil were to act as a chain transfer agent, then it would follow the following mathematical relationship (see appendix for derivation)

$$\log_{10}\frac{Qd}{Qd_0} = 2.303\, K_3\left(\frac{K_1}{K_4}\right)^{1/2}[M]t$$

Qd = concentration of chloranil at time t

Qd_0 = original concentration chloranil

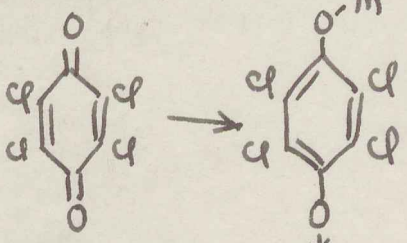
A possible mechanism for the action of chloranil as an inhibitor would be as follows:-

(9) $M^* +$  $\rightarrow$  $+ M^* \rightarrow$ 

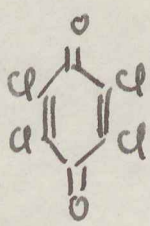
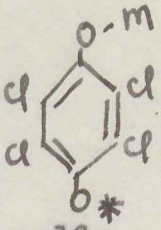
If this mechanism were correct then each chloranil would be capable of destroying two free radicals. Evidence given latter in this report would favor a mechanism of this sort. The equivalent rate constants are obtained for quinone and chloranil using a value of 2 for "y". (The number of growing chains destroyed by each molecule of inhibitor). To conclude, it looks very much as though in a vacuum chloranil is functioning as an inhibitor, although a small amount of chain transfer may be taking place.

In air, the plot of chloranil concentration with time seems to give two straight lines of different slope. The rate of disappearance of chloranil in air during the first part of the induction period is the same as the rate of disappearance of chloranil in vacuum.

(a) $M^{*} + O_2 \longrightarrow M\text{-}O\text{-}O^{*}$

(b) $M\text{-}O\text{-}O^{*}$ +  $+ O_2 \xrightarrow{etc.}$

(c) $M\text{-}O\text{-}O^{*} + M^{*} \longrightarrow M\text{-}O\text{-}O\text{-}M$

(d) M^{*} +   $\longrightarrow$ etc.

This could be accounted for if, for some reason or other, reaction (a) above where slow at first and then after five hours became important. During this first five hours, the rate determining reaction would be (d). After the first five hours reaction (a) would be very fast, and inhibition would occur by reaction (b) and (c) occurring simultaneously and at the same rate.

An alternate explanation of the results with chloranil in air is obtained from a plot of log Q against time. This plot is nearly linear which would indicate that in air chloranil is a chain transfer agent.

The function of chloranil in air is inconclusive. Additional data will be needed to decide whether the reaction is zero order of first order with respect to chloranil and, in turn, whether chloranil is an inhibitor or a chain transfer agent in air.

CALCULATIONS

Part I - Determination of rate constant for initiation stage from vacuum run data of p-benzoquinone in styrene

(a) $Q = Q_o - \frac{1}{2} k_1 [m]^2 t$

(b) $\frac{dQ}{dt} = -\frac{1}{2} k_1 [m]^2$

Note: $\frac{dQ}{dt}$ from graphs 1 and 2

$$\frac{dQ}{dt} = \frac{1 \times 10^{-2} \frac{\text{mols}}{\text{Liter}}}{13.6 \text{ hours}} = 7.35 \times 10^{-4} \frac{\text{mols}}{\text{Liter-hour}}$$

this value of $\frac{dq}{dt}$ represents the rate of disappearance of p-benzoquinone in styrene in a vacuum. Substituting this value in (a)

$$7.35 \times 10^{-4} \frac{\text{mols}}{\text{Liter-hour}} = -\frac{1}{2} k_1 [m]^2$$

(M) can be calculated from the following

Density of Styrene = 0.91 $\frac{\text{Grams}}{\text{m.l.}}$

1 Liter Styrene = 910 Grams

Therefore, a liter of styrene (assuming 100% purity is equivalent to

$$\frac{910}{104\ (\text{mol. weight})} = 8.75 \text{ molar}$$

thus:

$$[m]^2 = 76.6 \text{ mols}^2$$

$$K_1 = \frac{-2\frac{dQ}{dt}}{[m]^2} = \frac{-2\left(7.35 \times 10^{-4} \frac{\text{mols}}{\text{liter-hour}}\right)}{76.6 \text{ mols}^2}$$

$$K_1 = -1.92 \times 10^{-5} \text{ mols}^{-1} \text{ liter}^{-1} \text{ hour}^{-1}$$

Part II- The rate of disappearance of p-benzoquinone in the air run is slower than in the vacuum run, either due to a reoxidation of hydroquinone type end product with the consequent regeneration of inhibitor or due to a simultaneous inhibition of free radicals by oxygen with the formation of peroxide end products.

Part III - Determination of rate constant of initiation stage from vacuum run of chloranil in styrene

$$Q = Q_0 - \tfrac{1}{2} k_1' [m]^2 t \quad \text{(assuming value of z for y)}$$

$$\frac{dQ}{dt} = -\tfrac{1}{2} k_1' [m]^2$$

Note: $\frac{dQ}{dt}$ from graph 9

$$\frac{dQ}{dt} = \frac{1 \times 10^{-2} \ \frac{\text{mols}}{\text{Liter}}}{12.6 \ \text{hours}} = 7.94 \times 10^{-4} \ \frac{\text{mols}}{\text{Liter-hour}}$$

this value of $\frac{dQ}{dt}$ represents the rate of disappearance of chloranil in styrene under vacuum conditions. Substituting this value in (a)

$$7.94 \times 10^{-4} \ \frac{\text{mols}}{\text{Liter-hour}} = -\tfrac{1}{2} k_1' \left(76.6 \ \text{mols}^2\right)$$

$$k_1' = -2.04 \times 10^{-5} \ \text{mols}^{-1} \ \text{liter}^{-1} \ \text{hour}^{-1}$$

EXPERIMENTAL DATA

Key:

t = time (in hours) when sample was removed from constant temperature oil bath.

T = transmission

$\log_{10} \frac{I}{T}$ = D = optical density

t_v = time for viscosity runs (in seconds)

$\frac{t_v}{t_s} = \frac{n}{n_s}$ = ratio of viscosity of sample and viscosity of of standard styrene sample

λ = wavelength (millimicrons) at which readings were taken

Run # I = 2.50×10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (vacuum run)

λ = 452 millimicrons

time for viscosity run of standard styrene sample.
= 102.4 seconds.

Sample	t	T	$\frac{I}{T}$	$\log_{10}\frac{I}{T}$	t_r	$\frac{n}{n_s} = \frac{t_v}{t_s}$
1	0	0.565	1.77	0.248	103.0	1.01
2	3	0.662	1.51	0.179	103.4	1.01
3	6	0.685	1.46	0.164	103.4	1.01
4	9	0.840	1.19	0.0755	103.0	1.01
5	12	0.891	1.12	0.0492	103.2	1.01
6	18	0.955	1.05	0.0212	high	--
7	24	0.970	1.03	0.0128	high	--

Run # 2 - 2.50×10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (vacuum run)

λ = 452 millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10}\frac{I}{T}$
1	0	0.565	1.81	0.258
2	3	0.661	1.51	0.179
3	5	0.698	1.43	0.155
4	9	0.855	1.17	0.0682
5	12	0.925	1.08	0.0334
6	22	0.975	1.03	0.0128
7	25	0.975	1.03	0.128

Ruh #3 - 2.50 x 10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (air run)

λ = 452 Milli microns

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$
1	0	0.560	1.78	0.250
2	3	0.600	1.66	0.220
3	7	0.660	1.51	0.179
4	10	0.710	1.41	0.149
5	15	0.755	1.32	0.121
6	18	0.840	1.19	0.0755
7	25	0.935	1.07	0.0290
8	30	0.935	1.07	0.0290

Run #4 - 2.50 x 10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (air run)

λ = 452 millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$
1	0	0.560	1.78	0.250
2	3	0.590	1.70	0.230
3	7	0.615	1.62	0.210
4	10	0.690	1.45	0.161
5	18	0.840	1.19	0.0755
6	25	0.935	1.07	0.0290
7	28	0.935	1.07	0.0290

Run # 5 - 2.50×10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (air run)

λ = 452 millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$
1	0	0.535	1.86	0.270
2	4	0.585	1.70	0.230
3	8	0.695	1.44	0.158
4	15	0.788	1.27	0.104
5	20	0.865	1.15	0.0607
6	25	0.935	1.07	0.0290
7	30	0.935	1.07	0.0290

Run # 6 - 2.50×10^{-3} mols benzoquinone in 250 m.l. of H-99 Styrene (air run)

λ = 452 Millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$	t_r	$\frac{n}{n_s} = \frac{t_r}{t_s}$
1	0	0.535	1.86	0.270	103.2	1.01
2	2	0.580	1.72	0.236	--	--
3	4	0.610	1.64	0.215	103.4	1.01
4	8	0.690	1.45	0.161	103.0	1.01
5	15	0.790	1.26	0.100	103.8	1.02
6	19	0.875	1.14	0.0569	103.8	1.02
7	25	0.935	1.07	0.0290	high	--
8	28	0.935	1.07	0.0290	high	--

Run # 7 - 2.50×10^{-3} mols chloranil in 250 m.l. of H-99 Styrene (air run)

λ = 520 millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{I_0}$
1	0	0.110	9.08	0.958
2	4	0.245	4.08	0.611
3	9	0.330	3.02	0.480
4	21	0.570	1.76	0.246
5	30	0.832	1.20	0.0792
6	35	0.988	1.01	0.0043
7	36	0.988	1.01	0.0043

Run # 8 - 2.50×10^{-3} mols chloranil in 250 m.l. of H-99 Styrene (air run)

λ = 520 millimicrons

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$	t_r	$\frac{n}{n} = \frac{t_r}{t_s}$
1	0	0.110	9.08	0.958	--	--
2	3	0.191	5.25	0.720	103.4	1.01
3	5	0.270	3.80	0.580	--	--
4	8	0.318	3.16	0.500	--	--
5	15	0.405	2.46	0.391	103.4	1.01
6	20	0.560	1.78	0.250	103.2	1.01
7	30	0.795	1.26	0.100	104.0	1.02
8	36	0.990	1.01	0.0043	high	--

Run # 9 - 2.50×10^{-3} mols chloranil in 250 m.l. H-99

Styrene (vacuum run)

λ = 520 millimicrons

= 102.4 seconds

Sample	t	T	$\frac{I}{T}$	$\log_{10} \frac{I}{T}$	t_r	$\frac{n}{n} = \frac{t_r}{t_s}$
1	0	0.117	8.52	0.930	103.0	1.01
2	4	0.208	4.79	0.680	103.2	1.01
3	6	0.315	3.16	0.500	103.2	1.01
4	8	0.445	2.24	0.350	103.0	1.01
5	11	0.725	1.38	0.140	103.2	1.01
6	15	0.950	1.05	0.0212	103.2	1.01
7	18	0.950	1.05	0.0212	high	--

SUMMARY

1. The rate constant for the initiation stage of uncatalyzed thermal polymerization of styrene has been calculated from data obtained from p-benzoquinone in styrene run in a vacuum.
2. The rate of disappearance of p-benzoquinone in styrene has been determined for air and vacuum runs.
3. Mechanisms for air and vacuum runs of p-benzoquinone in styrene have been suggested, based upon the experimental data.
4. The rate constant for the initiation stage of uncatalyzed thermal polymerization of styrene has been calculated from data obtained from chloranil in styrene, run in a vacuum.
5. The rate of disappearance of chloranil in styrene has been determined for vacuum runs.
6. Mechanisms for vacuum runs of chloranil in styrene have been suggested, based upon the experimental data.
7. Not enough data is available to draw conclusions concerning the nature of the mechanism of air runs of chloranil in styrene.

APPENDIX

Derivation of chain transfer rate equations:

As in the case of the developement of equations for p-benzoquinone, in the thermal polymerization of styrene, the four steps of polymerization are discussed,

(1) Initiation:

$$2M \xrightarrow{K_1'} M^*$$

$$\frac{d[M^*]}{dt} = K_1'[M]^2$$

(2) Propagation:

$$M^* + M \xrightarrow{K_2'} MM^*$$

$$-\frac{d[M^*]}{dt} = K_3'[M^*][Qd]$$

(3) Chain Transfer:

$$M^* + Qd \xrightarrow{K_3'} MQd + d^*$$

$$\frac{dd^*}{dt} = K_3'[M^*][Qd]$$

OR

$$-\frac{d[M^*]}{dt} = \frac{dd^*}{dt}$$

M = monomer concentration

M^* = free radical

Qd = chloranil

K' = rate constant

(4) Termination :

$$m^* + m^* \xrightarrow{k_4'} m\text{-}m$$

$$-\frac{d[m^*]}{dt} = k_4'[m^*]^2$$

$$\frac{d[m^* + d^*]}{dt} = k_1'[m]^2 + k_3'[m^*][Qd] - k_4'[m^*]^2 - k_3'[m^*][Qd]$$

$$\frac{d[m^* + d^*]}{dt} = 0$$

at steady state:

$$k_1'[m]^2 = k_4'[m^*]^2$$

$$[m^*] = \left(\frac{k_1'}{k_4'}\right)^{1/2}[m]$$

$$\frac{d[Qd]}{dt} = k_3'[m^*][Qd]$$

$$\frac{d[Qd]}{dt} = k_3'\left(\frac{k_1'}{k_4'}\right)^{1/2}[m][Qd]$$

$$\frac{d[Qd]}{dt} = K_3' \left(\frac{K_1'}{K_4'}\right)^{\frac{1}{2}} [m]\, dt$$

$$\int_{Qd_0}^{Qd} \frac{d[Qd]}{[Qd]} = K_3' \left(\frac{K_1'}{K_4'}\right)^{1/2} [m] \int_{t_0}^{t} dt$$

$$\log_{10} \frac{Qd}{Qd_0} = 2.303\, K_3' \left(\frac{K_1'}{K_4'}\right)^{1/2} [m]\, t$$

This indicates that if chloranil acted soley as a chain transfer agent, the disappearance of chloranil in sytrene would follow a Logarithmic plot. The data is not conclusive on this point, thus it is suggest that:

(a) The reaction may be of an inhibitory nature in vacuum (with chloranil) and

(b) The reaction may consist of inhibition in two different ways in air.

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EXPERIMENTAL

The styrene used was obtained from the Dow Chemical Company and contained 85 parts per million of tertiary butylcatechol, the primary impurity. This sample of styrene was designated with the code H-99. Earlier exploratory work was done with styrene showing a different analysis of tertiary butylcatechol (10 parts per million) but all work here used the H-99 sample. The p-benzoquinone, chloranil, p-nitrosodimethyl aniline and p-nitrosodiethyl aniline were all obtained from Eastman Kodak and used directly without further purification. Stock solutions of inhibitor were prepared and used within one week. The concentrations of all stock solutions were 2.5 x 10-3 mols of inhibitor per 250 m.l. of styrene. (Unless otherwise indicated.)

Reaction tubes were prepared from 10 and 12 mm pyrex glass tubing, sealed on one end, and tested for leaks under water. Chloranil runs were made in the 10 mm glass tubing, using the special tips shown in diagram 7. The quinone runs were made in 12 mm pyrex glass tubing and attached to the evacuating apparatus as indicated in the inset in diagram 7. Before each run, the tubes were cleaned with dichromate solution, rinsed in acetone and dried. 10 ml of stock solution was then pipetted into each each tube and the tube (with sample in it) immersed in a bath of dry ice and acetone. When the sample

was frozen, the tubes were sealed off. (See special section for sealing off reaction tubes under vacuum, using apparatus in diagram I). The sealed samples were then removed from the dry ice-acetone bath, allowed to come to room temperature, and then placed in a constant temperature oil bath (210° F ± 0.5°) The time of immersion in the oil bath was recorded. Samples were then withdrawn at indicated intervals, placed immediately in the dry ice-acetone bath, and the seal broken. The sample was then brought up to room temperature, and divided into two portions. One was used for spectrophotometric measurements, and the other for viscosity measurements.

All spectrophotometric data was taken on a Cenco-Sheard Spectrophotolometer. The instrument is adapted for special tubes which hold the solution under examination (see drawing A). The readings were made with reference to pure styrence at a wavelength of 452 millimicrons for quinone and 520 millimicrons for chloranil. These particular value for a "reference wavelength" were determined by preparing solutions of various concentrations of each inhibitor and taking complete absorption curves (in the vesible spectrum) of each concentration. The wavelength at which greatest separation of the curves was coupled with maximum sensitivity, was chosen as a reference wavelength. (see graphs) To determine concentrations of chloraniland quinone as functions of Beer's Law, known concentrations of each inhibitor were prepared and the optical density determined for each concentration at the respective "reference wavelengths" This data is used to convert optical

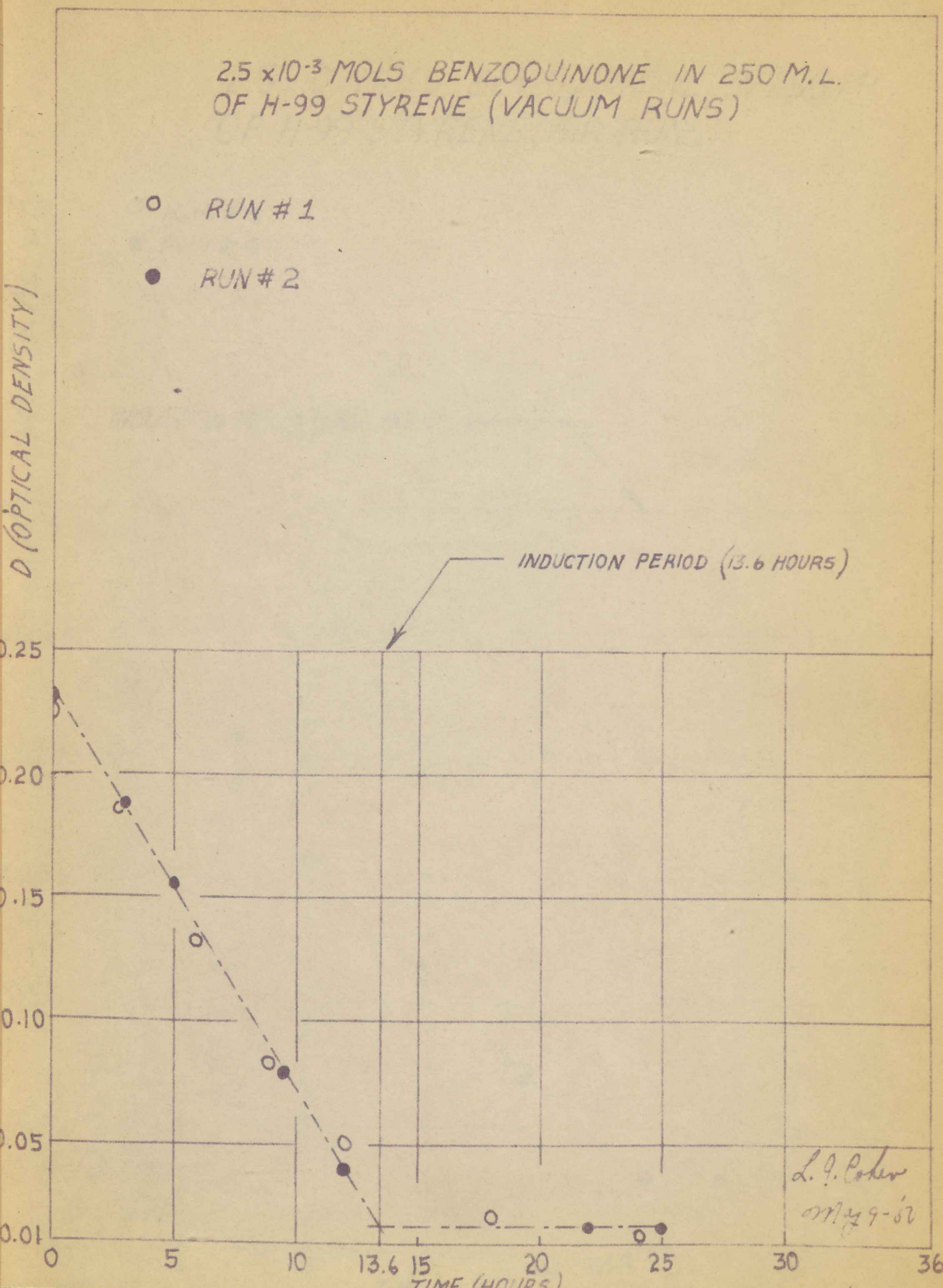
density readings of the various runs to values of concentration of inhibitor (see section on calculations)

Viscosity measurements were carried out in an Ostwald viscometer immersed in a constant temperature water bath. (This was regulated by a mercury contact thermoregulator which kept the bath at 25.00° ± 0.01°) The ostwald viscometer has the disadvantage of not being practical for very viscous solutions. However, this work was mainly concerned with a study of the viscosity during the induction period, and just at the end of the period. For this work, the viscometer worked very well. Five c.c. of the sample taken from the oil bath was pipetted into the viscometer, and the sample allowed to come to the temperature of the bath. Four readings for each sample were taken and the average time calculated (the time should not vary more than ± 0.2 second for each reading). The time of flow for a 5 c.c. sample of pure styrene was also determined and the ratio of viscosity of sample to viscosity of styrene calculated. After each determination, the viscometer was rinsed with acetone, partially dried by drawing air through the capillary, and baking at 110° C for 10 minutes. The viscometer was then allowed to come to room temperature before further measurements were taken.

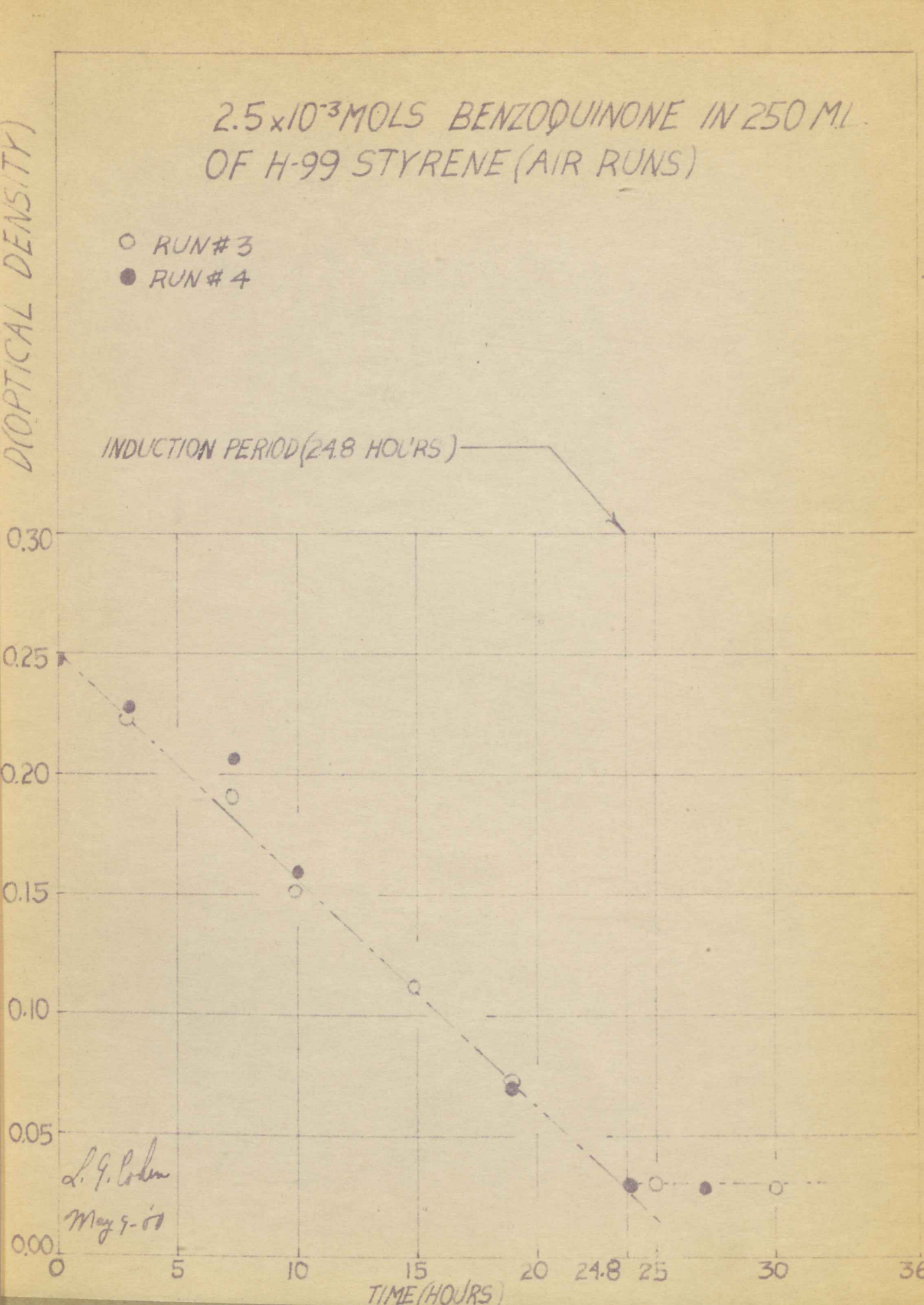
Special proceedure for evacuating reaction tubes:

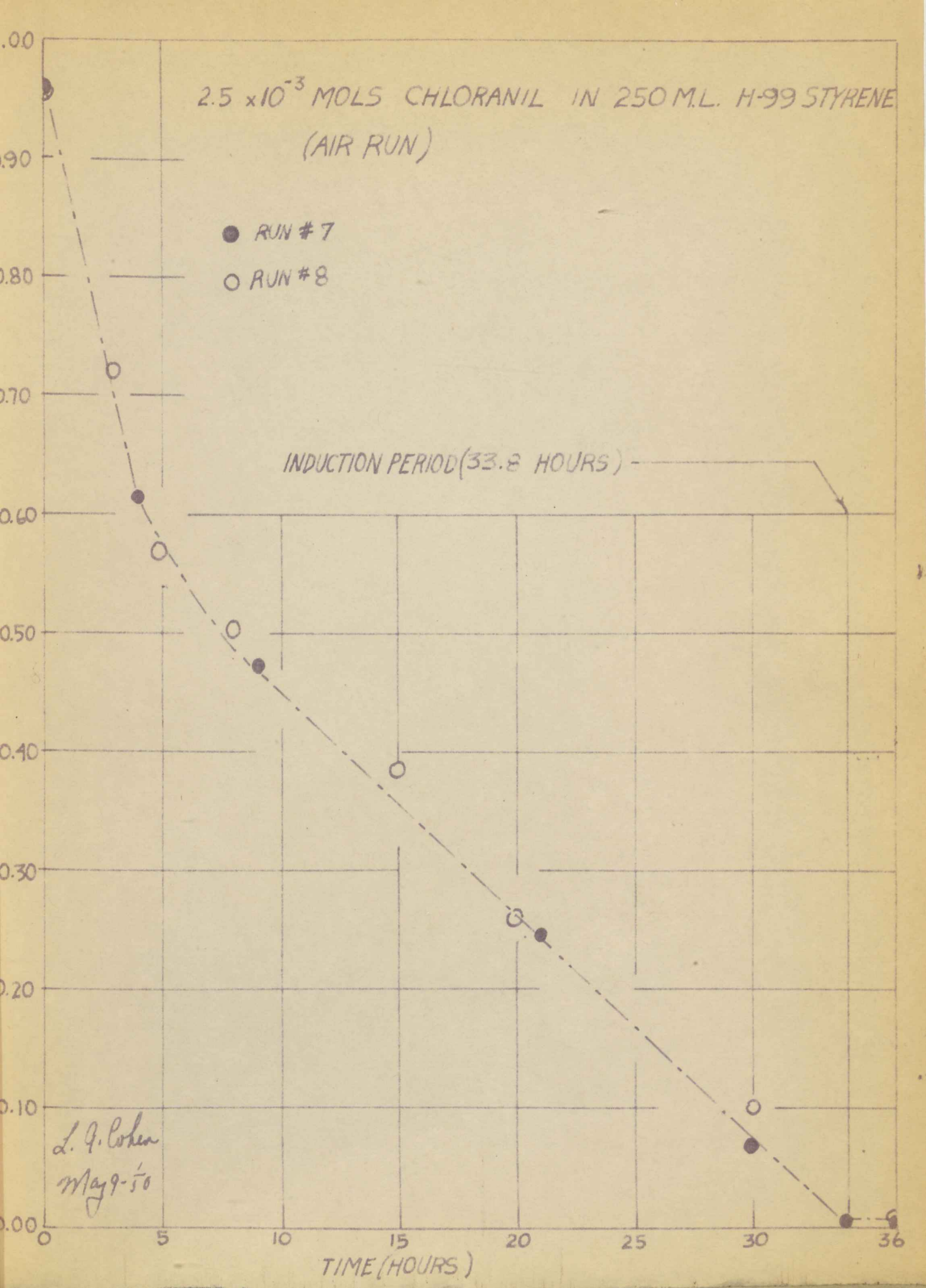
10 m.l. of the stock solution was pipetted into the reaction tubes as frozen, as before, in a dry ice-acetone bath. The special tip (see diagram I inserts) was inserted in the top of the reaction tube and sealed with Dekohtinsky cement. With the

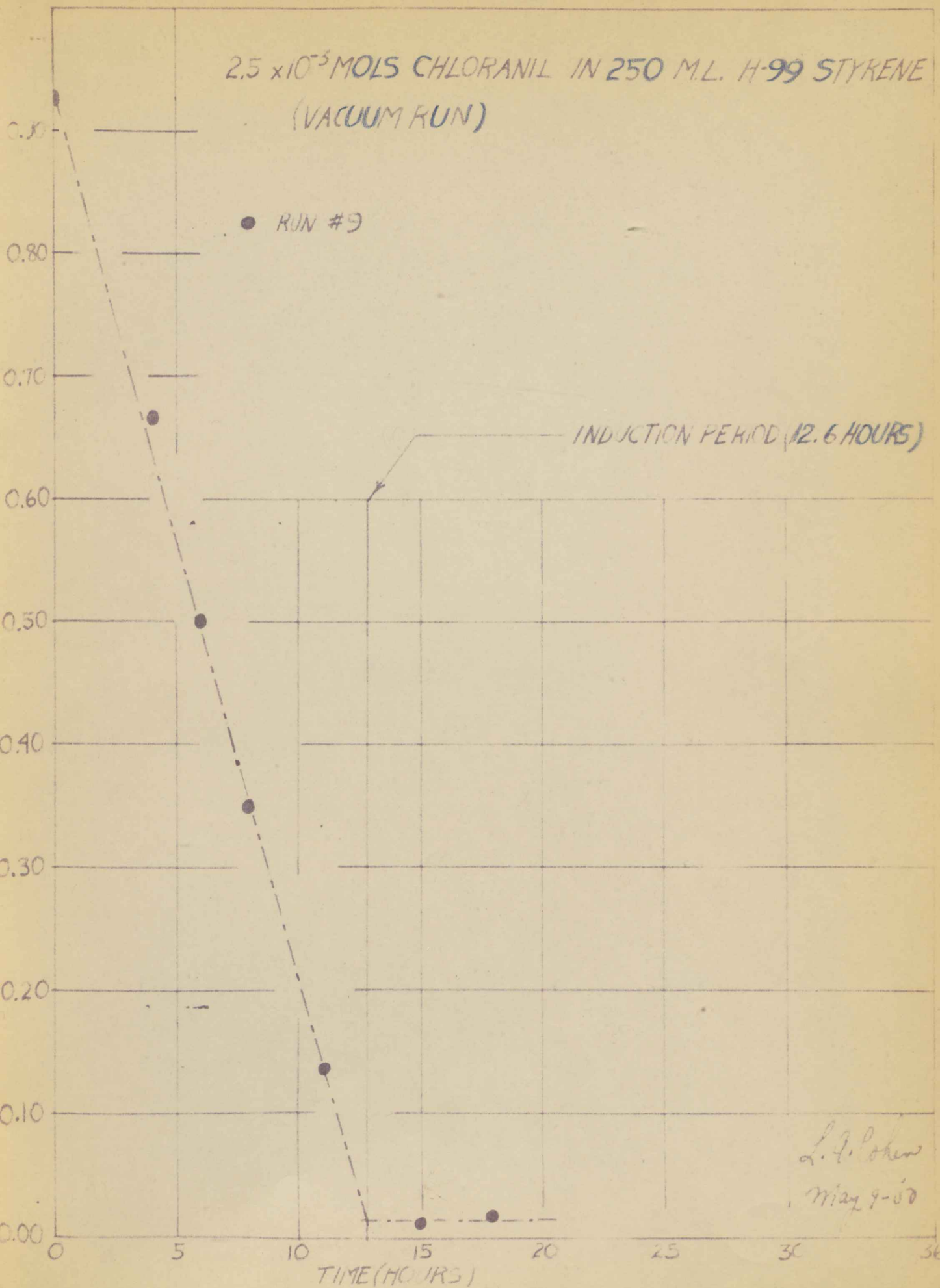
reaction tubes still in the dry ice acetone bath, valve (F) and valve (E) were closed. The vacuum pump was then turned on. Valve (F) was kept closed until the monometer reached a minimum. (About 1 m.m. with the pump used in this work) Clamp H was opened first, to admit nitrogen, then valve F was opened, admitting the nitrogen to the whole system. By grasping the rubber tubing at T, the nitrogen could be forced momentarily into the reaction tube. Valve F was then closed first, and clamp H closed. The evacuation continued as before, and the complete cycle repeated three times. Just prior to the sealing off of the tubes, valves E and F should be closed, and clamp H should be closed. It is suggested that a clamp be placed over each lead going to the reaction tubes and then each clamp be closed, one at a time, just prior to the sealing of each reaction tube, since the reaction tubes under vacuum tend to "implode" easily when the glass has been softened. If such a clamp has been tightly closed, any such accident will not affect other reaction tubes.

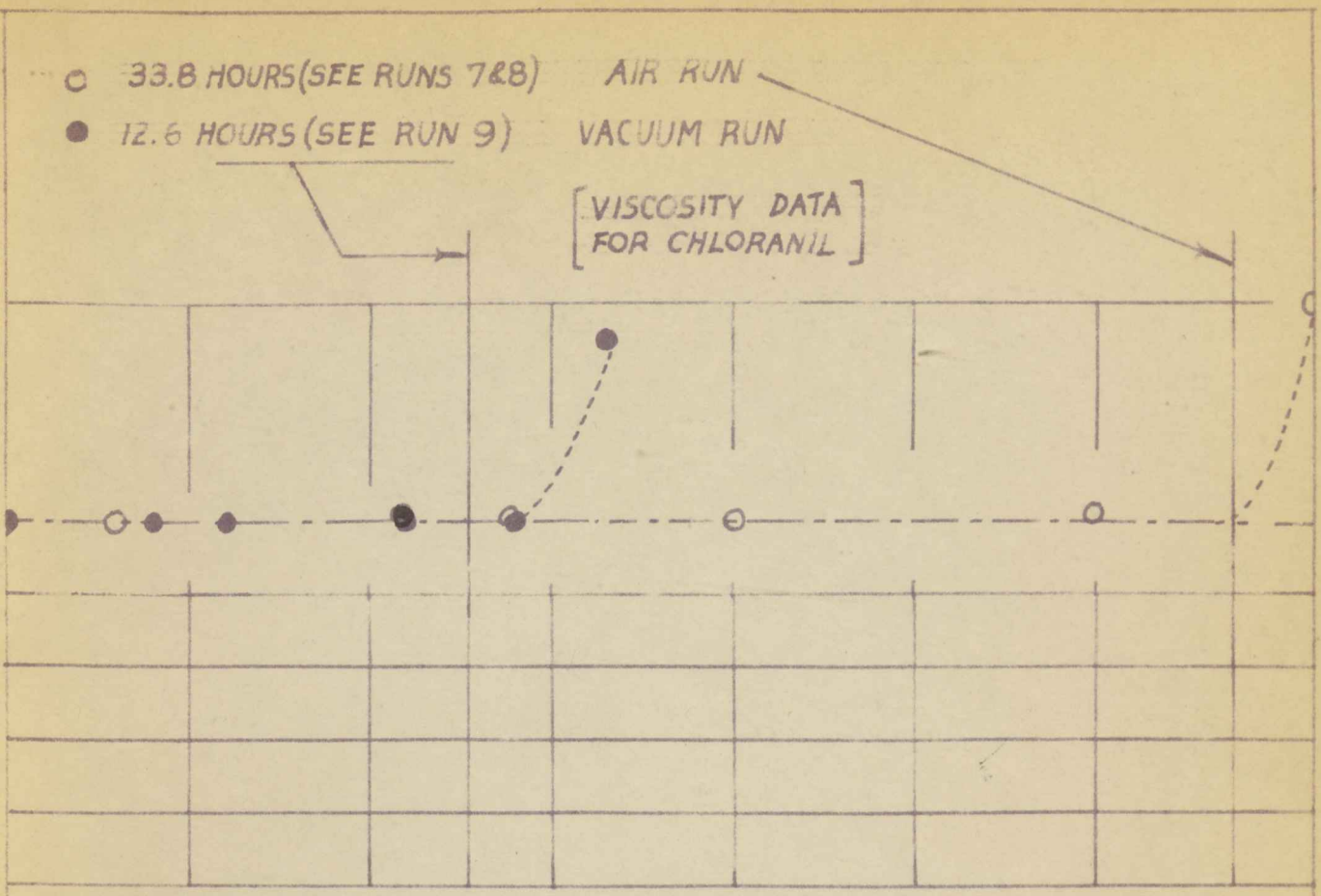

2.5 x 10⁻³ MOLS BENZOQUINONE IN 250 M.L. OF H-99 STYRENE (VACUUM RUNS)
RUN # 1
RUN # 2
D (OPTICAL DENSITY)
INDUCTION PERIOD (13.6 HOURS)
0.25
0.20
0.15
0.10
0.05
0.01
0
5
10
13.6
15
20
25
30
36
TIME (HOURS)
L. J. Cohen
May 9-62

2.5×10^{-3} MOLS BENZOQUINONE IN 250 M.l. OF H-99 STYRENE (AIR RUNS)



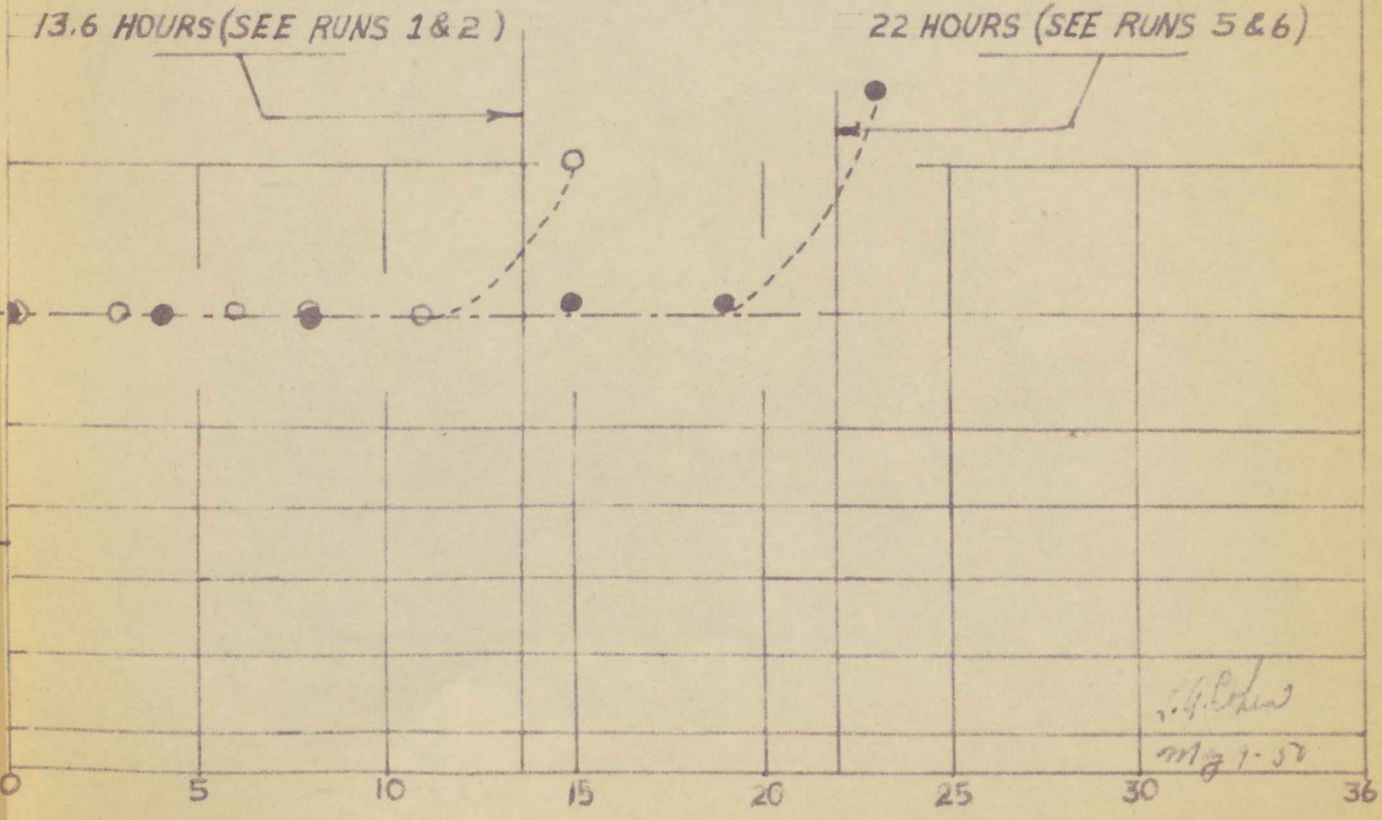

2.5 x10⁻³ MOLS CHLORANIL IN 250 M.L. H-99 STYRENE
(AIR RUN)
RUN #7
RUN #8
INDUCTION PERIOD (33.8 HOURS)
.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
.00
0
5
10
15
20
25
30
36
TIME (HOURS)
L. G. Cohen
May 9-50

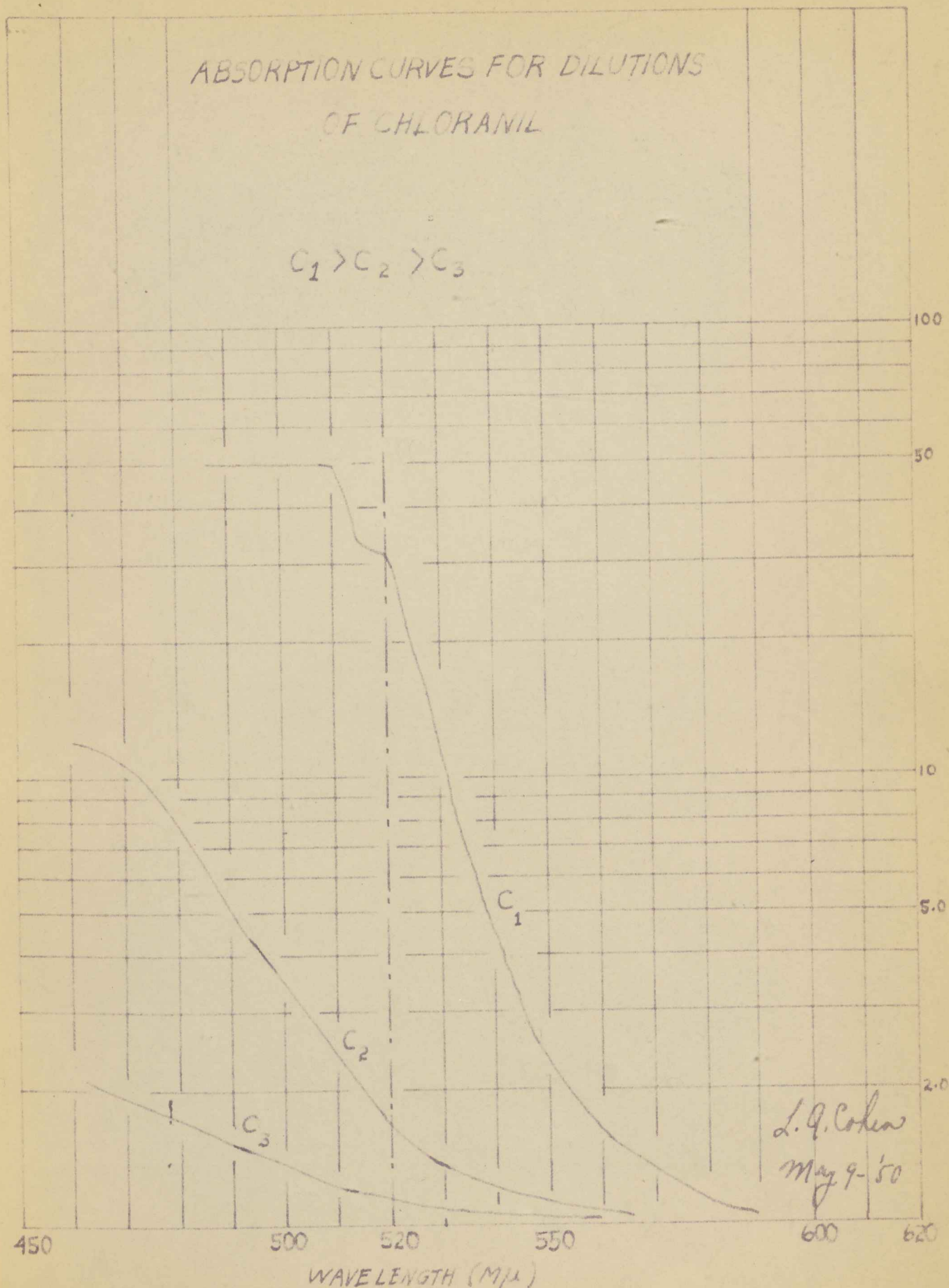

2.5 x 10⁻³ MOLS CHLORANIL IN 250 M.L. H-99 STYRENE
(VACUUM RUN)
RUN #9
INDUCTION PERIOD (12.6 HOURS)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
5
10
15
20
25
30
35
TIME (HOURS)
L. J. Poker
May 9-60



○ VACUUM RUN
● AIR RUN

VISCOSITY DATA FOR BENZOQUINONE




ABSORPTION CURVES FOR DILUTIONS
OF CHLORANIL
$C_1 > C_2 > C_3$
100
50
10
5.0
2.0
D (OPTICAL DENSITY)
C_1
C_2
C_3
L. Q. Cohen
May 9- '50
450
500
520
550
600
620
WAVE LENGTH (Mμ)

APPARATUS FOR THE EVACUATION OF REACTION TUBES (VACUUM RUNS)

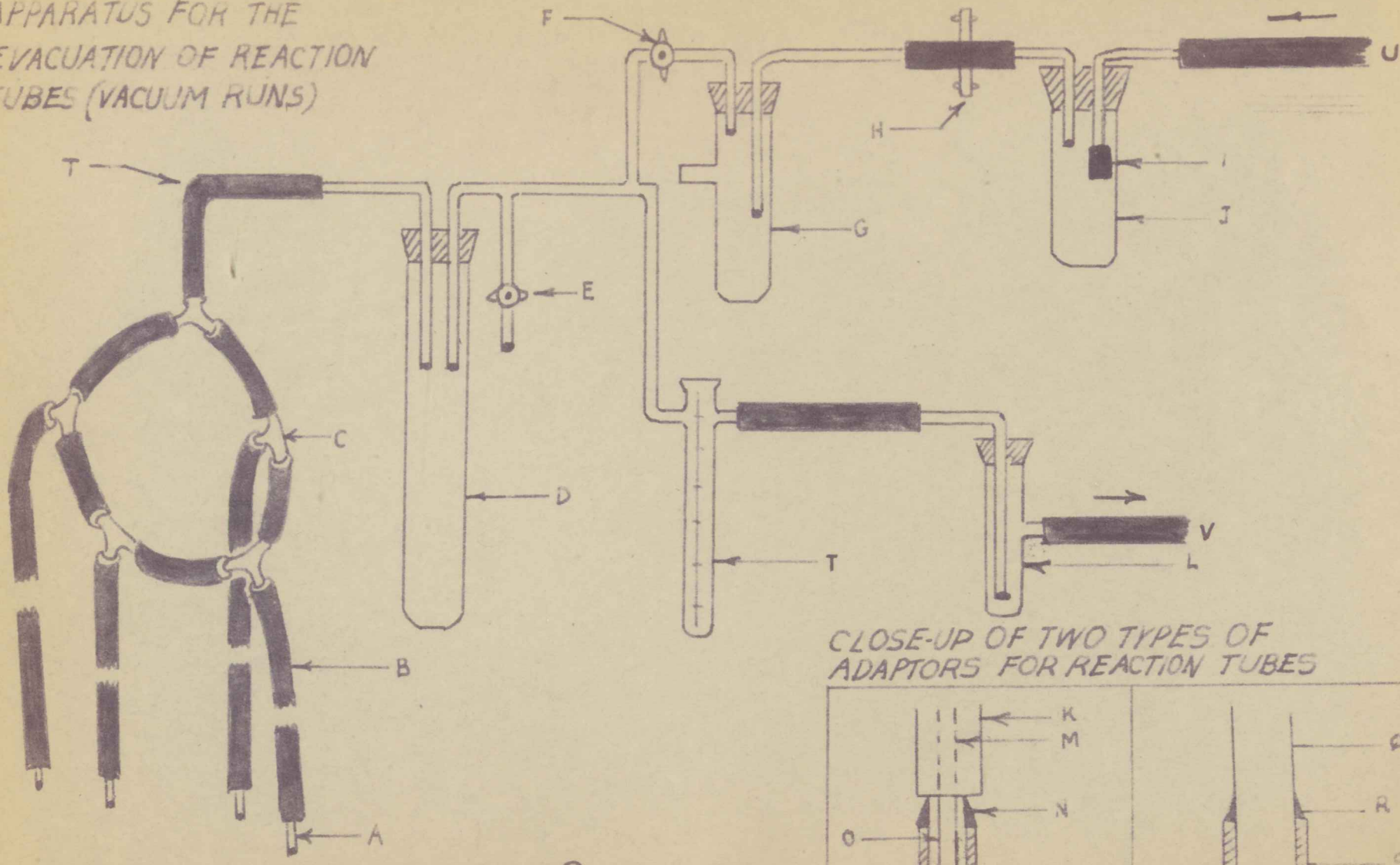
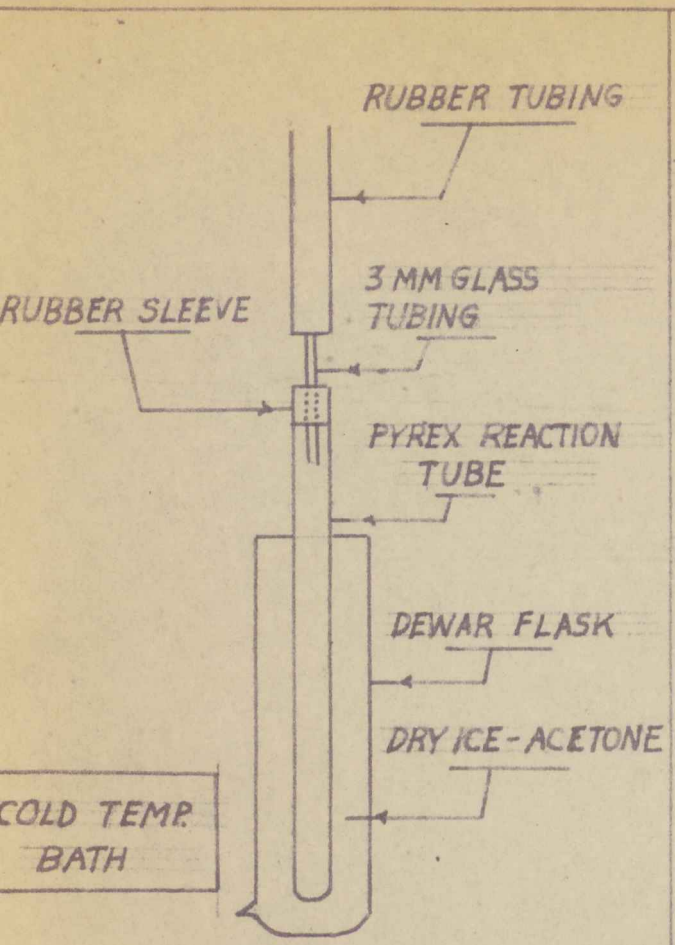
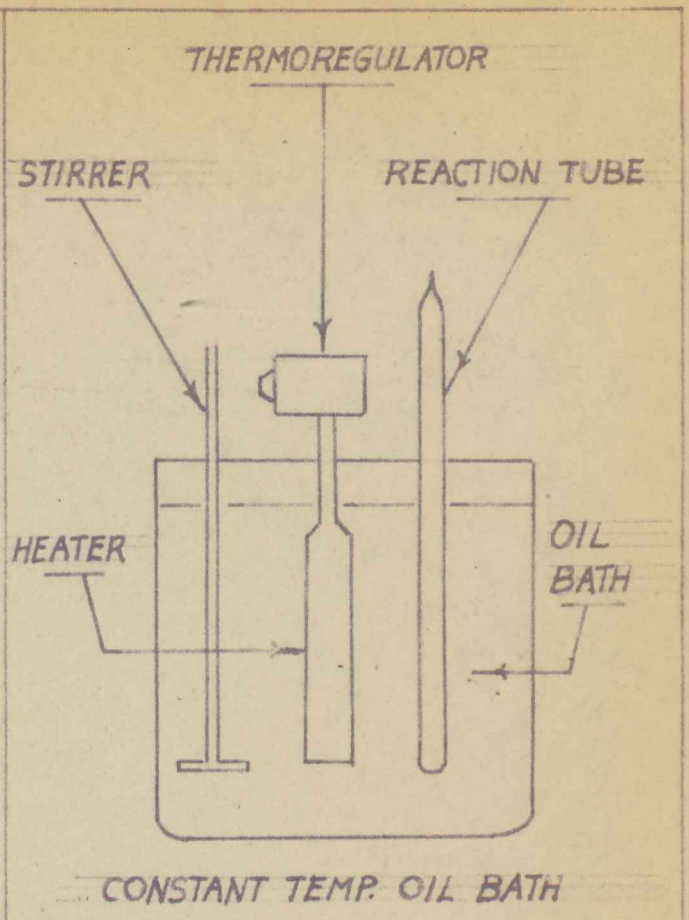


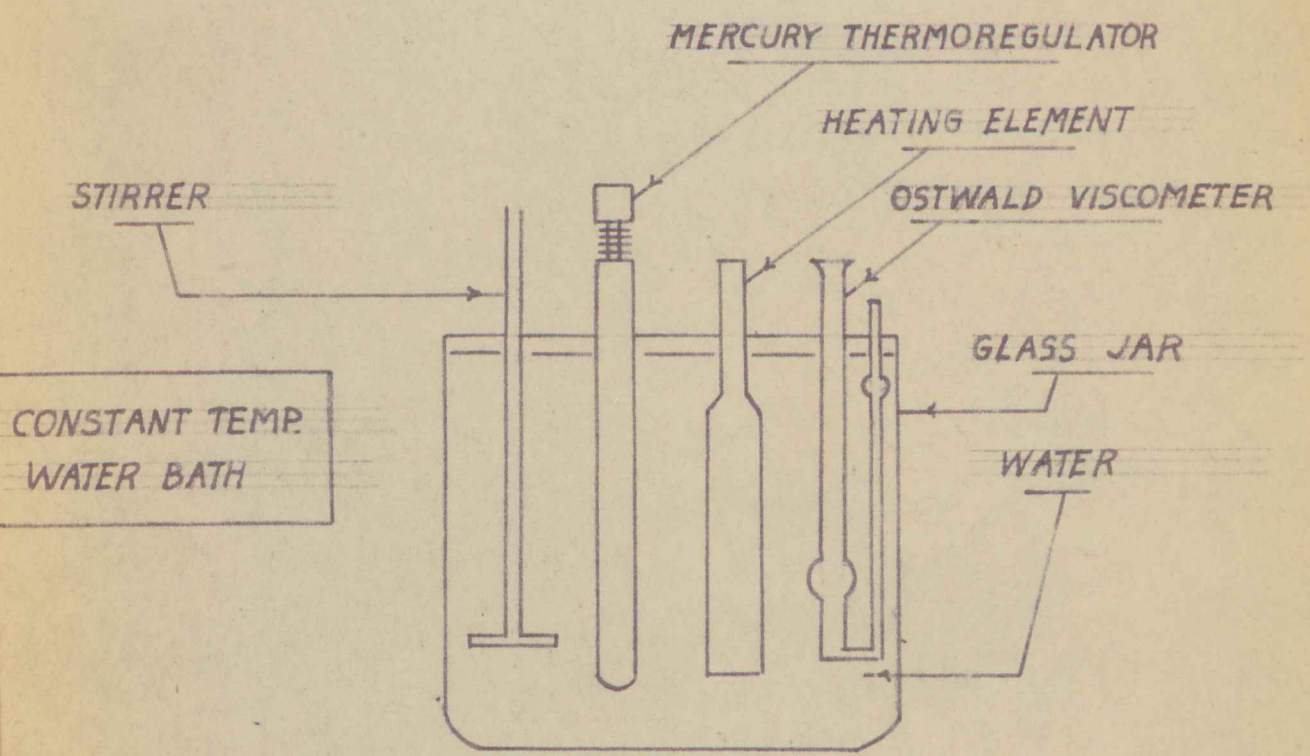
FIG. (1)

CLOSE-UP OF TWO TYPES OF ADAPTORS FOR REACTION TUBES

L. G. Cohen - May 9, 1950.







L. G. Cohen - 5/9/50